Investigations into Ni5Ga3/SiO2 intermetallic catalysts for CO2 hydrogenation: synthesis and characterization

Sharafutdinov, Irek; Elkjær, Christian Fink; Damsgaard, Christian Danvad; Gardini, Diego; Chiarello, Gian-Luca; Wallace, Pereira de Carvalho Hudson; Grundwaldt, Jan-Dierk

Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

CASE

Catalysis for Sustainable Energy

Investigations into Ni_5Ga_3/SiO_2 intermetallic catalysts for CO_2 hydrogenation: synthesis and characterization

Irek Sharafutdinov[1], Christian Fink Elkjær[1], Christian D. Damsgaard[2], Diego Gardini[2], Gian-Luca Chiarello[3], Pereira de Carvalho Hudson Wallace[3], Jan-Dierk Grundwaldt[3], Søren Dahl[1]

[1]Department of Physics Building 307, Technical University of Denmark, DK-2800 Lyngby, Denmark
[2]Center for Electron Nanoscopy, Technical University of Denmark, DK-2800 Lyngby, Denmark
[3]Institute for Chemical Technology and Polymer Chemistry, Karlsruher Institute of Technology (KIT), Engesserstr. 20, D-76131 Karlsruhe

Motivation

• Recently, an increasing attention has been drawn towards the utilization of alloys and intermetallic compounds for catalytic purposes: in the number of applications, they represent attractive alternatives to conventional catalysts in terms of cost, activity, stability and selectivity. In the fuel cells applications, Pt-Y alloy based catalysts were shown to possess enhanced activity compared to pure Pt [1]. For the selective semi-hydrogenation of acetylene to ethylene, Pd-Ga intermetallic catalysts were found to be more selective and resistant to coking compared to industrially used Pd-Ag [2]. Another example is Pt-Bi intermetallic compound, used in the anode side of the formic acid fuel cells: it is believed to have superior activity and CO tolerance with respect to pure platinum [3].

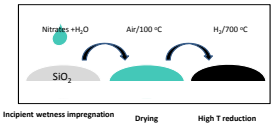
• However, despite the existence of a huge variety of intermetallic phases, a major challenge is to prepare well-defined supported nanoparticles in a sustainable and reproducible way [4]. Here we show that supported NiGa and Ni_5Ga_3 catalysts, which have been previously shown to be active and selective towards CO_2 hydrogenation to form CH_3OH, can be prepared following simple impregnation method.

Catalyst preparation

• A mixed aqueous solution of nickel and gallium nitrates was impregnated on high surface area silica (incipient wetness impregnation)

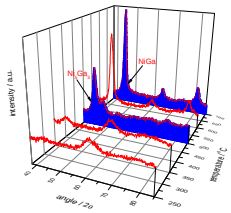
• Precursor dried and aged in air for 24 hours at 100-120ºC

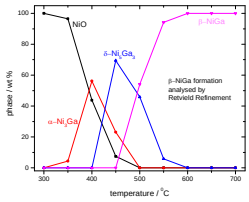
• Reduced in pure hydrogen flow for 2 hours at 700ºC to form the Ni-Ga alloy.



• In-situ Temperature Programmed Reduction & X-ray Diffraction of NiGa/SiO_2 and Ni_5Ga_3 catalysts

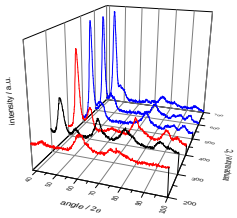
Experimental design: catalyst precursor is subjected to TPR in 90% H_2/He mixture. XRD scans are recorded at constant temperatures (high quality 2 hour scans)

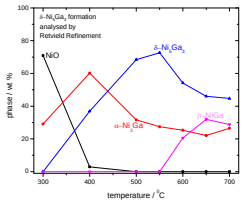




• *β-NiGa* phase formation proceeds through intermediate δ-Ni_5Ga_3 and α`-Ni_3Ga [5,6] formation at 500ºC. At 600ºC, complete transformation into β-NiGa is observed.

• Alloying proceeds through more Ni-rich phases

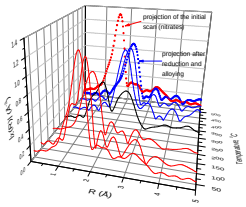




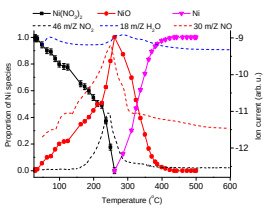
• *δ-Ni_5Ga_3* formation is a more complex process; alloying starts with α`-$Ni_3Ga$ phase formation. At 500ºC, *δ-$Ni_5Ga_3$* is prevailing. Further, a mixture of δ-$Ni_5Ga_3$, α`-Ni_3Ga and *β-NiGa* phases is observed

• Formation of an intermetallic phase from Ni_5Ga_3 precursor: in situ X-ray Absorption Spectroscopy

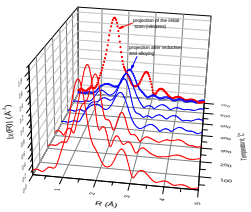
FT of EXAFS at Nickel K-edge



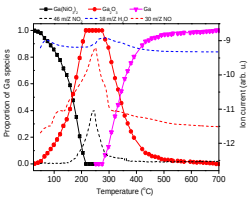
Linear combination fitting in the nickel NEXAFS region



FT of EXAFS at Gallium K-edge



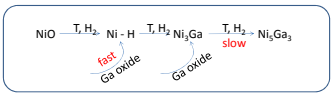
Linear combination fitting in the Gallium NEXAFS region



• Both nickel and gallium local structure starts to change close to 300°C (compare with in-situ XRD spectra and Retveld Refinement above)

• Nickel and gallium are reduced almost simultaneously

• Proposed mechanism of alloying



- Nickel and gallium nitrates are decomposed to oxides
- Reduction of gallium is slightly delayed:
  - NiO is reduced to nickel
  - Ga_2O_3 is immediately reduced and alloyed on the nickel surface to form Ni_3Ga
- As temperature is increased, gallium oxide is further reduced and incorporated into the structure of intermetallic compound

• References

1 – J. Greeley, *Nature Chemistry* 1, 552 - 556 (2009)
2 – Y. Grin, *Science and Technology of Advanced Materials* 8, 420-427 (2007)
3 – X. Ji, *Nature Chemistry* 2, 286 - 293 (2010)
4 – J. Chris Bauer, *J. Mater. Chem.* 18, 275–282 (2008)
5 – H. Okamoto, Journal of Phase Equilibria and Diffusion, 31, 6, 575-576 (2010)
6 – C. Bartholomew, Applied catalysis A: General 212, 17-60 (2001)

Acknowledgements
This research was supported by the Office of Science of the U.S. Department of Energy through the SUNCAT Center for Interface Science and Catalysis at SLAC/Stanford, from the Danish Ministry of Science and Innovation through the Catalysis for Sustainable Energy Initiative (CASE) at DTU and by The Danish National Research Foundation through CINF DTU.
The A. P. Møller and Chastine Mc-Kinney Møller Foundation is gratefully acknowledged for its contribution towards the establishment of the Center for Electron Nanoscopy in the Technical University of Denmark.